UNDERSTANDING THE NON-GAUSSIAN NATURE OF REACTIVE SOLUTE TRANSPORT. FROM PARTICLE DYNAMICS TO THE PARTIAL DIFFERENTIAL EQUATIONS

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ABSTRACT. In the present study we examine non-Gaussian spreading of solutes subject to advection, dispersion and kinetic sorption (adsorption/desorption). We start considering the behavior of a single particle and apply a random walk to describe advection/dispersion plus a Markov chain to describe kinetic sorption. We show in a rigorous way that this model leads to a set of differential equations. For this combination of stochastic processes such a derivation is new. Then, to illustrate the mechanism that leads to non-Gaussian spreading we analyze this set of equations at first leaving out the Gaussian dispersion term (microdispersion). The set of equations now transforms to the telegrapher's equation. Characteristic for this system is a longitudinal spreading, that becomes Gaussian only in the long-time limit. We refer to this as kinetics induced spreading. When the microdispersion process is included back again, the characteristics of the telegraph equations are still present. Now two spreading phenomena are active, the Gaussian microdispersive spreading plus the kinetics induced non-Gaussian spreading. In the long run the latter becomes Gaussian as well. Another non-Gaussian feature shows itself in the 2D situation. Here, the lateral spread and the longitudinal displacement are no longer independent, as should be the case for a 2D Gaussian spreading process. In a displacing plume this interdependence is displayed as a 'tailing' effect. We also analyze marginal and conditional moments, which confirm this result. With respect to effective properties (velocity and dispersion) we conclude that effective parameters can be defined properly only for large times (asymptotic times). In the two-dimensional case it appears that the transverse spreading depends on the longitudinal coordinate. This results in 'cigar-shaped' contours.

Keywords: Advection-diffusion equation and kinetic adsorption and random walk and Markov chain and solute transport and telegraph equation.

1. INTRODUCTION

It is well known that in the field a contaminant plume spreads at a higher rate than as predicted by theory and lab experiments. In addition, one observes that the spreading pattern often deviates from the Gaussian pattern, especially at early times (tailing). These phenomena have been analyzed intensively, theoretically, numerically and by field experiments ([15], [28], [7], [11], [12]), [30], [3], [24]). The majority of papers on this subject attribute these phenomena to the heterogeneity of the medium. In our paper we show that in a homogeneous aquifer a similar behavior occurs when contaminants are subject to a relatively slow kinetic adsorption/desorption reaction.

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We consider a homogeneous medium and follow a (solute) particle during its motion through the pore system, while simultaneously it is subject to adsorption/desorption. Although the porous medium itself is simply homogeneous and non-stochastic, the particle's behavior is still chaotic and, therefore, our particle model will be stochastic. Note that our approach differs from that of papers on particle tracking in the sense that we do not start with the advection-dispersion-reaction equations and, accordingly, perform a particle tracking algorithm to solve or simulate the equations. Instead, we start with a stochastic description for the movement of a single particle and work our way towards the differential equations. Particle tracking papers assume an analogy between particle tracking and the differential equations either by just stating the validity of this analogy or by referring to previous papers on particle tracking. To our knowledge a rigorous derivation of the differential equations for advective-dispersive transport with kinetic sorption starting from a stochastic model for a single particle does not exist in any of those papers.

We also discuss particle models used in various other fields, such as the velocity jump model (chemotaxis or movement of bacteria, Hillel). This velocity jump model (Giddings-Eyring model) leads to a telegraph equation. It differs from our model by the fact that there is no diffusion or dispersion phenomenon. We will demonstrate that, when the velocity jump is extended with dispersion/diffusion, the telegraph character stills remains. This explains the non-Gaussian behavior in the pre-asymptotic stage.

The non-Gaussian features can also be illustrated by (spatial) moments, especially by the third (skewness) and fourth (kurtosis) centralized moments. For the 1D situation first and second moments were studied by previous authors e.g. [34], [6] and [31]. These papers mainly focused on the large time (asymptotic) results. Pre-asymptotic expressions for first and second moments were first derived by [27]. Unfortunately, in the formulation of the solutions Michalak and Kitanidis suggest that for an arbitrary initial distribution of the phases the mean and variance in each separate phase can be obtained by a linear combination. However, this is only true for the non-centralized moments, but not for the variance. Moreover, one of the 4 solutions is incorrect (see section 5.1, also [10]). In our paper we shall consider the moments for the 2D situation and examine in detail the conditional moments. These moments manifest more clearly the non-Gaussian behavior than the 1D or marginal moments. It shows that non-Gaussian behavior can exist, even when the marginal moments suggest that the behavior is Gaussian.

In our 'particle view' the behavior of a particle is described by a random walk and a two state Markov process. A similar model was used by [34], [35] and [37]. Equivalent processes occur in other fields, such as chromatography ([17], [16], [22]) or in statistical physics (e.g. [14], [18], [21], [39] and [26]). The amount of literature related to this topic is extensive and spreads over many different fields. Here, we look at this topic from the perspective of solute transport in groundwater.

2. The particle view

2.1. **A stochastic particle model.** We model the movement of a single particle subject to an advection/dispersion/sorption process over a time interval $[0, t]$. For simplicity we discuss the one-dimensional case. We discretize time by choosing some n, and by dividing $[0, t]$ into n intervals of length $\Delta t = t/n$. We observe the

state of the particle at the time points $0, \Delta t, 2\Delta t, \ldots, n\Delta t$. For this state there are two possibilities: 'free' or 'adsorbed,' which we code by the letters f and a. The particle can only move when it is 'free,' and its displacement has two components: dispersion and advection.

Let X_k be the displacement due to the dispersion of the particle the kth time that it is 'free.' We model the X_k as independent random variables with mean and variance

$$\mathrm{E}\,[X_k] = 0 \quad \text{and} \quad \mathrm{Var}\,(X_k) = 2D\Delta t.$$

The displacement due to advection is given by $v\Delta t$, where v is the (deterministic) advection velocity.

Let K_n be the number of intervals $[k\Delta t, (k+1)\Delta t)$ during $[0,t]$ that the particle was 'free.' (Here the open bracket at the right end indicates that the point $(k+1)\Delta t$ is not included.) In other words, $K_n\Delta t$ is the free residence time of the particle in $[0,t]$. Let $S(t)$ be the position of the particle at time t. Combining the two types of displacement we obtain

$$S(t) = \sum_{k=1}^{K_n}(X_k + v\Delta t).$$

The distribution of K_n is determined by the kinetics, i.e., by the switching between the 'free' and the 'adsorbed' state. This is naturally described by a two state Markov chain. The state-transitions of this chain after a certain time step Δt are given by a transition probability matrix (p_{ij}):

$$\left[\begin{array}{cc} p_{ff} & p_{fa} \\ p_{af} & p_{aa} \end{array}\right] = \left[\begin{array}{cc} 1-b & b \\ a & 1-a \end{array}\right].$$

This means that for instance the transition from 'adsorbed' to 'free' has probability $a = p_{af}$ to happen during the time interval $[k\Delta t, (k+1)\Delta t)$ (note that actually we make this change—if it takes place—at the end of the interval).

We will be mainly interested in the moments of $S(t)$. Below we will compute the first and second moment, and in the next Section we discuss the (centered) third and fourth moment. To compute $\mathrm{E}\,[S(t)]$ we use the well known formula (see e.g. [29]) for a random sum of K_n independent and identically distributed random variables Y_k (also independent of K_n):

$$\mathrm{E}\left[\sum_{k=1}^{K_n}Y_k\right] = \mathrm{E}\,[K_n]\,\mathrm{E}\,[Y_1].$$

Here the mean of K_n equals: $\mathrm{E}\,[K_n] = \frac{a}{a+b}\,n$. This expression can be obtained from [38], or [10]. Substituting we find (with $n\Delta t = t$)

$$\mathrm{E}\,[S(t)] = \mathrm{E}\,[K_n]\,(\mathrm{E}\,[X_1 + v\Delta t]) = \frac{a}{a+b}\,vt.$$

Here, $(a+b)/a$ is the retardation factor R. To see this, note that the probability vector $\big(b/(a+b) \quad a/(a+b)\big)$ is the stationary distribution of the Markov chain, and so $a/(a+b)$ is the fraction of time the particle is free. Thus the effective velocity $v^* = v/R$. We have implicitly required that the particle at time 0 is given the state 'adsorbed' or 'free' according to this distribution, for other initial distributions there will be a correction term in the formula for $\mathrm{E}\,[S(t)]$, which tends to 0 as t tends to infinity (cf. [10]).

To compute $\mathrm{Var}\,(S(t))$ we use the well known formula (see e.g. [29]) for the *variance* of a random sum of K_n i.i.d. random variables Y_k (also independent of K_n):

$$(1) \qquad \mathrm{Var}\left(\sum_{k=1}^{K_n} Y_k\right) = \mathrm{E}\,[K_n]\,\mathrm{Var}\,(Y_1) + \mathrm{Var}\,(K_n)\,(\mathrm{E}\,[Y_1])^2.$$

This yields with $Y_k = X_k + v\Delta t$ and $n\Delta t = t$:

$$(2) \qquad \begin{aligned} \mathrm{Var}\,(S(t)) &= \mathrm{E}\,[K_n]\,\mathrm{Var}\,(X_k + v\Delta t) + \mathrm{Var}\,(K_n)\,(\mathrm{E}\,[X_k + v\Delta t])^2 \\ &= \frac{a}{a+b}\,2D\,t + \mathrm{Var}\,(K_n)\,v^2(\Delta t)^2, \end{aligned}$$

where (as can be deduced from [38] or [10])

$$(3) \qquad \mathrm{Var}\,(K_n) = \frac{ab(2-a-b)}{(a+b)^3}\,n - \frac{2ab(1-a-b)}{(a+b)^4}[1-(1-a-b)^n].$$

The equations (2) and (3) thus tell us that the variance of the displacement of the particle grows more or less linearly in time with (asymptotic) slope

$$\frac{a}{a+b}2D + \frac{ab(2-a-b)}{(a+b)^3}v^2\Delta t.$$

2.2. Skewness and kurtosis.
To obtain the skewness of $S(t)$ we must use the not so well known formula for the *third central moment* of a random sum of K_n i.i.d. random variables Y_k (also independent of K_n):

$$\begin{aligned} \mathrm{E}\left[\left(S(t) - \mathrm{E}\,[S(t)]\right)^3\right] &= \mathrm{E}\left[\left(\sum_{k=1}^{K_n} Y_k - \mathrm{E}\left[\sum_{k=1}^{K_n} Y_k\right]\right)^3\right] \\ &= \mathrm{E}\,[K_n]\,\mathrm{E}\left[(Y_1 - \mathrm{E}\,[Y_1])^3\right] + 3\mathrm{E}\,[Y_1]\,\mathrm{Var}\,(Y_1)\,\mathrm{Var}\,(K_n) \\ &\quad + (\mathrm{E}\,[Y_1])^3\,\mathrm{E}\left[(K_n - \mathrm{E}\,[K_n])^3\right]. \end{aligned}$$

To actually derive a formula for the skewness of the displacement of the particle from this equation will lead to very heavy computations (and the situation for the kurtosis is even worse). However, without doing any computations we can already tell that as $t \to \infty$ the skewness must tend to zero, and the kurtosis to 3: this is because the distribution of the displacement of the particle will tend to a Gaussian by the Central Limit Theorem for *random* sums of independent identically distributed random variables. In our case this follows since K_n/n tends in the mean, and hence in probability to $a/(a+b)$, see [13], page 258.

2.3. Decreasing the time steps.
The discrete time steps are somewhat unnatural. We would like to let Δt tend to 0. But then we have to realize that a and b are functions of Δt. Since the probability that the particle changes its state is proportional to the time Δt it is observed (if Δt is not too large), we should put

$$a = \mu\Delta t, \qquad b = \lambda\Delta t,$$

where μ and λ are now the *rates* at which the particle switches from 'adsorbed' to 'free', and from 'free' to 'adsorbed'. Substituting this in Eqs (2) and (3), we obtain

$$\mathrm{Var}\,(S(t)) = \frac{\mu}{\lambda+\mu}2Dt + \frac{\lambda\mu(2-(\lambda+\mu)\Delta t)}{(\lambda+\mu)^3}v^2t$$
$$- \frac{2\lambda\mu(1-(\lambda+\mu)\Delta t)}{(\lambda+\mu)^4}\left[1-\left(1-(\lambda+\mu)\frac{t}{n}\right)^n\right]v^2.$$

Letting $\Delta t \to 0$, and hence $n \to \infty$ we obtain

$$\mathrm{Var}\,(S(t)) = \frac{\mu}{\lambda+\mu}2Dt + \frac{2\lambda\mu}{(\lambda+\mu)^3}v^2t - \frac{2\lambda\mu}{(\lambda+\mu)^4}\left[1-\mathrm{e}^{-(\lambda+\mu)t}\right]v^2.$$

Thus we recuperate a (more general and more detailed) version of the main result of [19], *and* there is a match with the expression that comes from the moment analysis based on the differential equations (as can be derived by correcting the results in [27]).

2.4. **The state of the particle at time t.** Let $S_f(t)$ be the position of the particle at time t *given* that it is free at time t.

To find the distribution of $S_f(t)$, we need the distribution of $K_n^{(f)}$, the number of intervals $[k\Delta t, (k+1)\Delta t)$ during $[0,t]$ that the particle was free, given that it is free at time $t = n\Delta t$. We find now (where $\mathrm{E}\left[K_n^{(f)}\right]$ can be deduced from [38]) that:

$$\mathrm{E}\,[S_f(t)] = \mathrm{E}\left[K_n^{(f)}\right]v\Delta t = \left[\frac{a}{a+b}n + \frac{b\,(1-(1-a-b)^n)}{(a+b)^2}\right]v\Delta t$$
$$= \frac{a}{a+b}vt + \frac{b\,(1-(1-a-b)^{t/\Delta t})}{(a+b)^2}v\Delta t.$$

Substituting $a = \mu\Delta t$, $b = \lambda\Delta t$, and letting $\Delta t \to 0$ we obtain

$$\mathrm{E}\,[S_f(t)] = \frac{\mu}{\lambda+\mu}vt + \frac{\lambda v}{(\lambda+\mu)^2}\left(1-\mathrm{e}^{-(\lambda+\mu)t}\right).$$

From [10] we have that $\mathrm{Var}\left(K_n^{(f)}\right)$ equals

$$\left[\frac{a\,b\,(2-a-b)}{(a+b)^3} + \frac{2\,b\,(a-b)\,(1-a-b)^n}{(a+b)^3}\right]n$$
$$+ \left[\frac{b\,(3\,a-b)}{(a+b)^3} - \frac{4\,a\,b}{(a+b)^4}\right][1-(1-a-b)^n] + \frac{b^2}{(a+b)^4}[1-(1-a-b)^{2\,n}].$$

Using Equation (1) we derive from this

$$\mathrm{Var}\,(S_f(t)) = \mathrm{E}\left[K_n^{(f)}\right]\mathrm{Var}\,(X_k+v\Delta t) + \mathrm{Var}\left(K_n^{(f)}\right)(\mathrm{E}\,[X_k+v\Delta t])^2$$
$$= \frac{a}{a+b}2Dt + \mathrm{Var}\left(K_n^{(f)}\right)v^2(\Delta t)^2 + \frac{b\,(1-(1-a-b))^{t/\Delta t}}{(a+b)^2}2D\Delta t.$$

Substituting $a = \mu\Delta t, b = \lambda\Delta t$, and letting $\Delta t \to 0$ we obtain

$$\text{Var}\,(S_f(t)) = \frac{\mu}{\lambda + \mu}\, 2Dt + \frac{\lambda}{(\lambda + \mu)^2}\left(1 - \mathrm{e}^{-(\lambda+\mu)t}\right) 2D$$

$$+ \left[\frac{2\lambda\mu}{(\lambda + \mu)^3} + \frac{2\lambda(\mu - \lambda)}{(\lambda + \mu)^3}\,\mathrm{e}^{-(\lambda+\mu)t}\right] v^2 t$$

$$- \frac{4\lambda\mu}{(\lambda + \mu)^4}\left[1 - \mathrm{e}^{-(\lambda+\mu)t}\right] v^2 + \frac{\lambda^2}{(\lambda + \mu)^4}\left[1 - \mathrm{e}^{-2(\lambda+\mu)t}\right] v^2.$$

It can be shown that this matches with the expressions in [27], when these are corrected as in [10]. Similar computations can be made for the displacement of the particle *given* that it is absorbed at time t.

2.5. **Derivation of the differential equations.** We will now show how the fundamental differential equations (9), (10) can be obtained from a diffusion limit of the single particle model. Our approach is similar to the one followed for transport in fluidized beds in [9]. In order to obtain this diffusion limit we also discretize space in locations

$$i\Delta x, \quad i = \ldots, -1, 0, 1, \ldots.$$

Here we let Δx depend on Δt in the classical way, which is motivated by the fact that typically at time t the spatial fluctuations are of order $\sqrt{t}$:

(4) $$\Delta x = c\sqrt{\Delta t},$$

where $c > 0$ will be chosen later. The particle moves according to a Markov chain (Z_n), which is a birth-death process (birth=one step to the right, death=one step to the left), with the additional possibility that the particle may become adsorbed and free again. The state space is therefore a product

$$S = \{\ldots, -1, 0, 1, \ldots\} \times \{a, f\},$$

where e.g. $Z_n = (i, a)$ means that at time $n\Delta t$ the particle is at $i\Delta x$, and is absorbed. Let β_i, δ_i and α_i be the probabilities that the particle (in the free state)
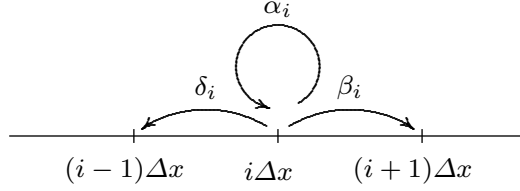

FIGURE 1. The three possible movements of the particle when it is free.

moves from $i\Delta x$ to $(i+1)\Delta x$, from $i\Delta x$ to $(i-1)\Delta x$, or stays at $i\Delta x$. Note that in this model the dispersion may depend on the location, i.e., we could more generally consider (deterministic) inhomogeneous media. To make this more realistic we could also let the adsorption and desorption rates depend on i. As we consider here only the homogeneous case, we take $\beta_i = \beta, \delta_i = \delta$ and $\alpha_i = \alpha$ for each i. To fit

the new model with the model in Section 2.1 we choose values for β, δ and α in the following fashion:

$$\beta = D\frac{\Delta t}{(\Delta x)^2} + \frac{v^2}{2}\left(\frac{\Delta t}{\Delta x}\right)^2 + \frac{v}{2}\frac{\Delta t}{\Delta x}$$

$$\delta = D\frac{\Delta t}{(\Delta x)^2} + \frac{v^2}{2}\left(\frac{\Delta t}{\Delta x}\right)^2 - \frac{v}{2}\frac{\Delta t}{\Delta x}$$

$$\alpha = 1 - \beta - \delta = 1 - 2D\frac{\Delta t}{(\Delta x)^2} - v^2\left(\frac{\Delta t}{\Delta x}\right)^2.$$

By fitting we mean that the mean and the variance of the displacement in a time interval of length Δt of the particle (in the free state) are the same in the two models. Indeed, the mean of this displacement equals $\beta\Delta x - \delta\Delta x = v\Delta t$, and the variance equals

$$\beta(\Delta x)^2 + \delta(\Delta x)^2 - (v\Delta t)^2 = 2D\Delta t.$$

In terms of Δt only, using (4), the displacement probabilities are

$$\beta = \frac{D}{c^2} + \frac{v^2\Delta t}{2c^2} + \frac{v\sqrt{\Delta t}}{2c}$$

$$\delta = \frac{D}{c^2} + \frac{v^2\Delta t}{2c^2} - \frac{v\sqrt{\Delta t}}{2c}$$

$$\alpha = 1 - \frac{2D}{c^2} - \frac{v^2\Delta t}{c^2}.$$

From this we see that these are indeed probabilities for Δt small enough, provided we choose $c > \sqrt{2D}$. The possible transitions of the chain are
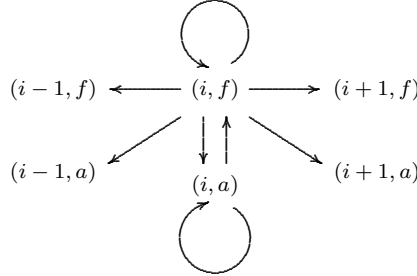
The corresponding transition probabilities are:

$p_{(i,f),(i+1,f)} = \beta(1 - \lambda\Delta t)$ $p_{(i,f),(i+1,a)} = \beta\lambda\Delta t$ $p_{(i,f),(i-1,f)} = \delta(1 - \lambda\Delta t)$
$p_{(i,f),(i-1,a)} = \delta\lambda\Delta t$ $p_{(i,a),(i,a)} = 1 - \mu\Delta t$ $p_{(i,a),(i,f)} = \mu\Delta t$
$p_{(i,f),(i,f)} = \alpha(1 - \lambda\Delta t)$ $p_{(i,f),(i,a)} = \alpha\lambda\Delta t$

Let $p_f(i,n)$, respectively $p_a(i,n)$, be the probability that at time $t = n\Delta t$ the particle is free, respectively absorbed and at position $i\Delta x$.
The master equations for the particle are

(5)
$$p_f(i, n+1) = p_f(i-1, n)\beta(1 - \lambda\Delta t) + p_f(i+1, n)\delta(1 - \lambda\Delta t)$$
$$+ p_f(i, n)\alpha(1 - \lambda\Delta t) + p_a(i, n)\mu\Delta t,$$

and

(6)
$$p_a(i, n+1) = p_f(i-1, n)\beta\lambda\Delta t + p_f(i+1, n)\delta\lambda\Delta t$$
$$+ p_f(i, n)\alpha\lambda\Delta t + p_a(i, n)(1 - \mu\Delta t).$$

With some abuse in notation regarding the functions p_a and p_f we will denote the limiting probabilities of $p_a(i, n)$ and $p_f(i, n)$ as $i\Delta x \to x$, and $t = n\Delta t$ by $p_a(x, t)$ and $p_f(x, t)$. We will obtain partial differential equations for these limiting probabilities when we let $\Delta t \to 0$, and $i = i(\Delta t) \to \infty$, in such a way that $i\Delta x \to x$. (The obvious way to achieve this is to take $i(\Delta t)$ equal to the integer closest to $x/(c\sqrt{\Delta t})$.) Rearranging (5) we obtain

(7)
$$p_f(i, n+1) = p_f(i-1, n)\beta + p_f(i+1, n)\delta + p_f(i, n)\alpha - \lambda\Delta t[p_f(i-1, n)\beta$$
$$+ p_f(i+1, n)\delta + p_f(i, n)\alpha] + p_a(i, n)\mu\Delta t.$$

In the first three terms of the right hand side we substitute the values for β, δ and α:

(8)
$$p_f(i-1, n)\beta + p_f(i+1, n)\delta + p_f(i, n)\alpha =$$
$$= \left[D\frac{\Delta t}{(\Delta x)^2} + \frac{v^2}{2}\left(\frac{\Delta t}{\Delta x}\right)^2\right]\left[p_f(i-1, n) - 2p_f(i, n) + p_f(i+1, n)\right]$$
$$+ \left[\frac{v}{2}\frac{\Delta t}{\Delta x}\right]\left[p_f(i-1, n) + p_f(i+1, n)\right] + p_f(i, n).$$

Substituting Equation (8) into (7) and dividing by Δt, we obtain an equation for the difference quotient $(p_f(i+1, n) - p_f(i, n))/\Delta t$. Then, letting $\Delta t \to 0$, we obtain

(9)
$$\frac{\partial p_f(x, t)}{\partial t} = D\frac{\partial^2 p_f(x, t)}{\partial x^2} - v\frac{\partial p_f(x, t)}{\partial x} - \lambda p_f(x, t) + \mu p_a(x, t).$$

For the adsorbed phase a similar equation can be derived. Here, since the adsorbed particle is not subject to advection or dispersion, the first and second term at the right hand side are absent.

(10)
$$\frac{\partial p_a(x, t)}{\partial t} = -\mu p_a(x, t) + \lambda p_f(x, t).$$

2.6. **From particle to plume.** It might seem surprising that we study the behavior of a contaminant plume from the stochastic analysis of a single particle. Here we illustrate how these two approaches are connected. We model the contaminant plume by a collection of N particles. These particles move independently according to the same law as the single particle considered in the previous sections. Let $S_i(t)$ be the position of the ith particle at time t. We are interested in the centroid $Z(t)$ of the plume at time t. This is given by

$$Z(t) = \frac{1}{N}\sum_{i=1}^{N} S_i(t).$$

We are also interested in the spreading of the plume around its centroid. This we measure by the (empirical) variance $V(t)$ of the particles given by

(11)
$$V(t) = \frac{1}{N}\sum_{i=1}^{N} (S_i(t) - Z(t))^2.$$

The random variable $Z(t)$ is an average of independent identically distributed random variables with finite expectation. Therefore by the strong law of large numbers for t fixed, and N large

(12)
$$Z(t) \approx \mathrm{E}\left[S(t)\right].$$

We now turn to the spread of the plume. Here the situation is more complicated because the terms in the sum are no longer independent random variables, and also depend on N. It is well known that a rewriting of Equation (11) yields

$$V(t) = \frac{1}{N}\sum_{i=1}^{N}\left(S_i(t) - Z(t)\right)^2 = \frac{1}{N}\sum_{i=1}^{N}\left(S_i(t) - \mathrm{E}\left[S(t)\right]\right)^2 - \left(Z(t) - \mathrm{E}\left[S(t)\right]\right)^2.$$

We have already argued (see (12)) that the last term is approximately 0, and another application of the law of large numbers to the first term yields that

$$V(t) \approx \mathrm{E}\left[\left(S(t) - \mathrm{E}\left[S(t)\right]\right)^2\right] = \mathrm{Var}\left(S(t)\right).$$

3. Giddings-Eyring Model

A simpler system, different from but still related to the system described by Eqs. (9) and (10), is given by the following equations:

$$\begin{aligned}
\frac{\partial N_f(x)}{\partial t} + v\frac{\partial N_f(x)}{\partial x} &= \mu N_a(x) - \lambda N_f(x) \\
\frac{\partial N_a(x)}{\partial t} &= \lambda N_f(x) - \mu N_a(x).
\end{aligned}$$

The difference is that the dispersion process is absent. This system is known in the literature under various names. In probability theory and statistical physics it is known as a persistent or correlated random walk and has been studied e.g. by [14], [18], [33], [21], and [39]. In the field of chromatography the system is intensively studied as well ([17], [16], [22]). Solutions for the probability density functions of the particles are given by Giddings and Eyring. [20], citeHillel applies the equations to the movement of bacteria in the direction of the gradient of food molecules (chemotaxis) and uses the term "velocity jump process". Several interesting observations can be made with respect to the spreading of the particles. The particles are undergoing an 'apparent' dispersion, despite the fact that (hydrodynamic) dispersion is not included in the model. This 'kinetics-induced' dispersion develops in a non-Gaussian way. In systems where both hydrodynamic dispersion and kinetics-induced dispersion are present, the latter sometimes can be more dominant, such that the non-Gaussian spreading is observed also in systems with hydrodynamic dispersion. We shall illustrate this later. First, we introduce a moving coordinate system with velocity v^*. The new x-coordinate is:

$$\bar{x} = x - v^* t,$$

where $v^* = v\mu/(\lambda + \mu)$. In the new coordinate system free particles move to the right with velocity $v_f = v - v^* = v\lambda/(\lambda + \mu)$. The adsorbed particles 'move' with velocity $v_a = -v^* = -v \times \mu/(\lambda + \mu)$. The minus sign indicates that the movement is to the left (i.e. with respect to the new coordinate system). The equations are

now:

$$\frac{\partial N_f(\bar{x})}{\partial t} + v_f \frac{\partial N_f(\bar{x})}{\partial \bar{x}} = \mu N_a(\bar{x}) - \lambda N_f(\bar{x})$$

$$\frac{\partial N_a(\bar{x})}{\partial t} + v_a \frac{\partial N_a(\bar{x})}{\partial \bar{x}} = \lambda N_f(\bar{x}) - \mu N_a(\bar{x}).$$

The equations can be rewritten as a single differential equation by considering first the sum and difference of the particle distributions (Kac's trick), i.e.,

$$u(x) = N_f(x) + N_a(x); \quad w(x) = N_f(x) - N_a(x).$$

After summation and substraction of the differential equations we obtain for u and w:

$$\frac{\partial u}{\partial t} + \left(\frac{\lambda - \mu}{\lambda + \mu}\right)\frac{v}{2}\frac{\partial u}{\partial \bar{x}} + \frac{v}{2}\frac{\partial w}{\partial \bar{x}} = 0$$

$$\frac{\partial w}{\partial t} + \left(\frac{\lambda - \mu}{\lambda + \mu}\right)\frac{v}{2}\frac{\partial w}{\partial \bar{x}} + \frac{v}{2}\frac{\partial u}{\partial \bar{x}} = -u(\lambda - \mu) - w(\lambda + \mu).$$

Now we differentiate the first equation to t, the second to $\bar{x}$ and eliminate the derivatives of w:

(13) $$\frac{\lambda\mu v^2}{(\lambda + \mu)^3}\frac{\partial^2 u}{\partial \bar{x}^2} - \frac{1}{\lambda + \mu}\frac{\partial^2 u}{\partial t^2} - \frac{v(\lambda - \mu)}{(\lambda + \mu)^2}\frac{\partial^2 u}{\partial t \partial \bar{x}} = \frac{\partial u}{\partial t}$$

This is a telegrapher's equation with an additional term due to asymmetry ($\mu \neq \lambda$). Hillel discusses the symmetrical ($\lambda = \mu$) case only, but Weiss ([39]) also makes some remarks on asymmetry. Also see Masoliver [26] and [5]. The telegraph equation may be interpreted either as a diffusion equation with a perturbation term that disappears at large times, or as a wave equation with a perturbation term that disappears at early times. Thus, as time proceeds, the system can be described by three different equations: first, a wave equation for early times; secondly, a telegraph equation for intermediate times and thirdly, an advection-dispersion equation for large times.

3.1. **Large time behavior and the advection-dispersion equation.** Hillel uses the following argument that leads to a useful result for large times. For large times the velocity $[LT^{-1}]$ and sorption rates $[T^{-1}]$ typically are expressed in large time units and thus their values become large. Then, the first term at the left hand side of (13) dominates over the second and third term. Therefore, at large times the equation approximately describes a dispersion process with an equivalent dispersion coefficient D^*, purely induced by the kinetics:

$$D^* = \frac{\lambda\mu v^2}{(\lambda + \mu)^3}.$$

3.2. **Short time behavior and the wave equation.** In a similar way it can be shown that for small times the terms at the left hand remain, while the right side becomes small. The remaining expression is a wave equation that can be written as:

$$\left[\frac{\partial}{\partial t} + \frac{\mu v}{\lambda + \mu}\frac{\partial}{\partial \bar{x}}\right]\left[\frac{\partial}{\partial t} - \frac{\lambda v}{\lambda + \mu}\frac{\partial}{\partial \bar{x}}\right]u = 0$$

For an initial pulse at $\bar{x} = 0$ the solution represents two pulses propagating along the characteristics. In $\bar{x}$-space,

$$\bar{x} - v_a t = 0, \qquad \bar{x} - v_f t = 0$$

which in x-space correspond to: $x = 0$, $x - vt = 0$.

These pulses can be identified as a stagnant pulse (the original adsorbed particles) and a travelling pulse (original free particles).

3.3. **Intermediate time behavior.** The wave equation and diffusion equation are approximations for the process at short and large times respectively. The intermediate time is described exactly by the full telegraphers's equation. Therefore, examination of the solutions to this equation will give information on the pre-asymptotic spreading behavior of this process.

Solutions for the distribution of the particles have been derived by [17], [16], and [22]. For detailed discussions of these functions see [36], [23] and [37].

Giddings and Eyring consider four types of densities $h_{ff}, h_{af}, h_{fa}, h_{aa}$:

(14)
$$
\begin{aligned}
h_{ff}(\tau, t) &= e^{-\lambda\tau - \mu(t-\tau)} \sqrt{\frac{\lambda\mu\tau}{t-\tau}} I_1(\theta) + e^{-\lambda t}\delta(t-\tau) \\
h_{fa}(\tau, t) &= \lambda e^{-\lambda\tau - \mu(t-\tau)} I_0(\theta) \\
h_{af}(\tau, t) &= \mu e^{-\lambda\tau - \mu(t-\tau)} I_0(\theta) \\
h_{aa}(\tau, t) &= e^{-\lambda\tau - \mu(t-\tau)} \sqrt{\frac{\lambda\mu(t-\tau)}{\tau}} I_1(\theta) + e^{-\mu t}\delta(\tau),
\end{aligned}
$$

where $\tau = x/v$, $\theta = 2\sqrt{\lambda\mu\tau(t-\tau)}$ and $I_0(\cdot)$ and $I_1(\cdot)$ are modified Bessel functions. Note that $\tau = x/v$ is not simply a convenient scaling of the x-coordinate, but τ also represents the residence time in the free phase. The expressions h_{ij} represent the probability densities of the free residence time for different phases and different initial states of the particles. The first index indicates the initial state of the particle and the second index indicates the state of the particles the pdf is referring to. The distributions are zero for $\tau < 0$ and $\tau > t$ ($x < 0$ and $x > vt$). The delta functions at $\tau = 0$ and $\tau = 0$ (which in x-space corresponds to $x = 0$ and $x = vt$) represent exponentially decreasing pulses and can also be identified as the fractions of particles that, since $t = 0$, did not (yet) perform a change of state.

In Figure 2 and 3 we present graphs with the evolution in time of these distributions, using as initial condition the (unit) pulse consisting of free and adsorbed particles in equilibrium. Let π_f and π_a be the initial amount of particles in each phase. Equilibrium exists for $\frac{\pi_f}{\pi_a} = \frac{\mu}{\lambda}$, and, if the total amount is unity we have:

$$\pi_a = \frac{\mu}{\lambda + \mu}; \quad \pi_f = \frac{\lambda}{\lambda + \mu}.$$

Thus, for $t = 0$:

$$N_f(x, t) = \pi_f \delta(x); \quad N_a(x, t) = \pi_a \delta(x).$$

We denote the residence distributions due to this initial condition as h_f^{eq} and h_a^{eq}:

(15)
$$
\begin{aligned}
h_f^{eq}(\tau, t) &= \pi_f h_{ff}(\tau, t) + \pi_a h_{af}(\tau, t) \\
h_a^{eq}(\tau, t) &= \pi_f h_{fa}(\tau, t) + \pi_a h_{aa}(\tau, t),
\end{aligned}
$$

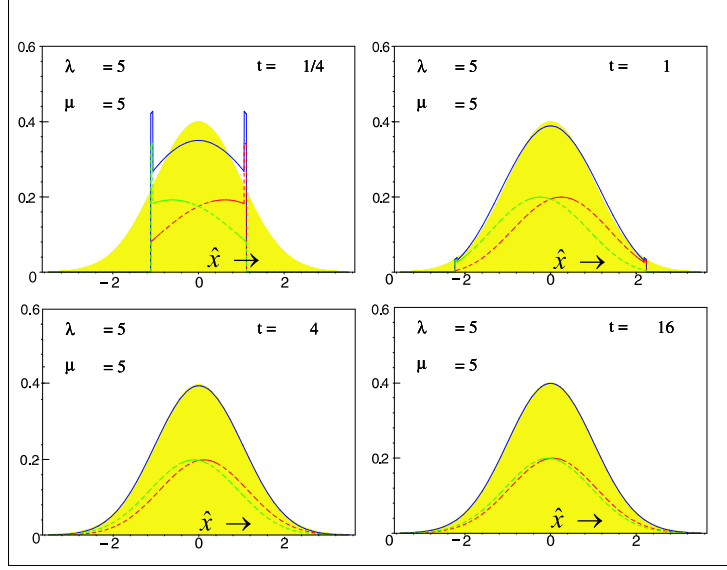while for the total amount of particles we have, $h_{tot}^{eq} = h_f^{eq} + h_a^{eq}$.

FIGURE 2. Distributions of separate phases and total plume at 4 moments in time. Symmetric case ($\lambda = \mu$). Solid (blue) line for total plume. Dashed lines for (green) adsorbed phase and (red) free phase, yellow background for Gaussian distribution.

In Figures 2 and 3 we compare distributions (15) and h_{tot}^{eq} with a Gaussian distribution with mean v^*t and variance $2D^*t$ representing the distribution of a solute with velocity v^* and dispersion D^*. All distributions are plotted versus a scaled variable $\hat{x}$:

$$\hat{x} = \frac{x - v^*t}{\sqrt{2D^*t}}.$$

Several stages of the system are shown. At early times ($t = 1/4$, Figure 2, upper left graph) the pulses of free and adsorbed mass are still distinguishable. The pulses move apart in $\hat{x}$ space and are damped. The mass that 'leaves' the pulses gradually fills the space in between and builds up a distribution that becomes Gaussian in the end (e.g., $t = 16$, Figure 2, lower right graph). The distribution in the interval between the pulses is absent in a pure wave system and is typical for the telegraph equation. In the final stage the pulses are completely damped and the distribution approaches the normal distribution. Summarized, at early times the 'wave-character' dominates, at large times the 'diffusion-character' dominates, while at intermediate times the system is adequately described by a telegraph equation (travelling and dampened pulses + mixed zone in between). For $\lambda = \mu$ the Gaussian distribution is reached slightly faster than in the asymmetric case ($\lambda \neq \mu$), as seen in Figure 3. For both cases the pulses disappear for t exceeding both $3/\lambda$ and $3/\mu$. In the next section local dispersion is included. We show that the two-dimensional distribution still may deviate from two-dimensional Gaussian functions even though the corresponding one-dimensional distribution is close to Gaussian.
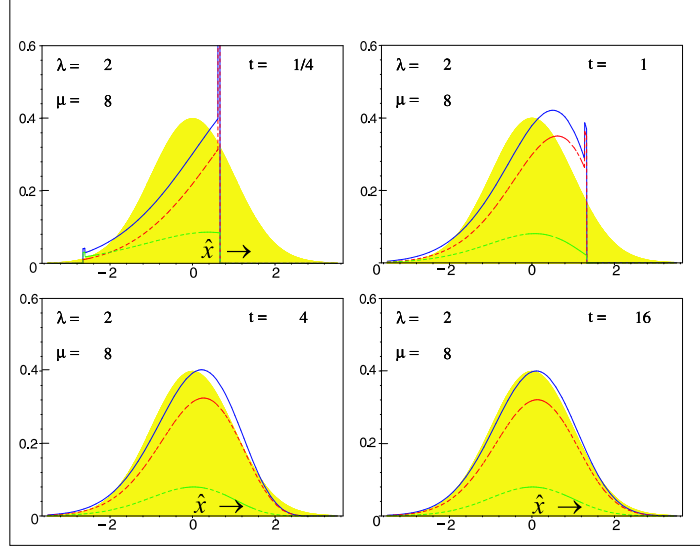
FIGURE 3. Distributions of separate phases and total plume at 4 moments in time. Asymmetric case ($\lambda \neq \mu$). Solid (blue) line for total plume. Dashed lines for (green) adsorbed phase and (red) free phase, yellow background for Gaussian distribution.

4. GIDDINGS-EYRING MODEL INCLUDING DISPERSION

We extend the Gidding-Eyring model by including longitudinal and transverse dispersion. This way we obtain the following two-dimensional system.

$$
\text{(16)} \qquad
\begin{aligned}
\frac{\partial N_f}{\partial t} - D_L \frac{\partial^2 N_f}{\partial x^2} - D_T \frac{\partial^2 N_f}{\partial y^2} + v \frac{\partial N_f}{\partial x} &= \mu N_a - \lambda N_f \\
\frac{\partial N_a}{\partial t} &= \lambda N_f - \mu N_a,
\end{aligned}
$$

where now N_f and N_f represent a two dimensional particle density distribution $[L^{-2}]$ and D_L and D_T are the longitudinal and transverse dispersion coefficients. We do not use different notations for the one- and two dimensional particle densities. We assume that their distinction will be clear from the context.

It appears that the effect of transverse dispersion is much more dramatic than that of longitudinal dispersion, while its solution is much easier to derive. Therefore, we analyze longitudinal and transverse dispersion separately and start by including transverse dispersion first.

4.1. **Transverse dispersion.** We use an approach proposed by [37]. Consider two distinct species, one adsorbing and one non-adsorbing. Let the spatial distribution of the non-adsorbing solute be given by $c(x, y, t)$. Further, let τ be the 'free residence time' of the adsorbing particles and let the distribution of τ at time t be $h_{ij}(\tau, t)$, i.e. for particles in phase j with an initial unit pulse in phase i (see by (14)). If the initial pulse is N_i^0, the particle fraction with free residence time τ at time t becomes

$N_i^0 h_{ij}(\tau, t)$, where $\tau < t$. The spatial distribution of this fraction is equal to that of the non-adsorbing particles at $t = \tau$, or: $dN_{ij}(x, y, t) = N_i^0 h_{ij}(\tau, t)c(x, y, \tau)d\tau$. Summing fractions with τ, $0 \leq \tau \leq t$, we obtain:

$$(17) \qquad N_{ij}(x, y, t) = N_i^0 \int_0^t h_{ij}(\tau, t)c(x, y, \tau) \, d\tau.$$

We apply Van Kooten's approach first to the case with only transverse dispersion. For a non-adsorbing solute with advection in the x-direction and dispersion in the y-direction (D_L is assumed zero) the distribution is:

$$c(x, y, t) = \frac{1}{2\sqrt{\pi D_T t}} \exp\left(-\frac{y^2}{4D_T t}\right) \delta(x - vt).$$

Insert this function in the integral (17). Because of the delta function the integral can be evaluated directly. After substitution of τ by x/v we obtain:

$$(18) \qquad N_{ij}(x, y, t) = N_i^0 \frac{h_{ij}(\frac{x}{v}, t)}{2\sqrt{\pi D_T \frac{x}{v}}} \exp\left(-\frac{y^2}{4D_T \frac{x}{v}}\right).$$

For a given value of x, expression (18) describes the distribution in y-direction of a certain amount of particles. The amount is equal to $N_i^0 h_{ij}(\frac{x}{v}, t)$ per unit of length in x-direction and it spreads in the y-direction as a Gaussian distribution with variance $2D_T \frac{x}{v}$. The transverse variance now depends on the x-coordinate, which is clearly in conflict with a 2D Gaussian distribution. The interdependence of transverse variance and x-coordinate can be understood by considering the residence times in the free phase. During the 'free phase' time particles travel in positive x-direction and simultaneously spread in the y-direction. At a given time t the particles that have spent more time in the free phase are found further along the x-direction. They are also more widely spread in y-direction, since they have been subject to dispersion for a longer time. Further, note that for $\frac{x}{v} > t$ the functions $h_{ij}(\frac{x}{v}, t)$ are zero. Therefore, $N_{ij}(x, y, t)$ is zero for $x > vt$.

In Figure 4 this is illustrated by 2D contours for unit initial pulses in the free and adsorbed phase. The following scaled coordinates are used:

$$(19) \qquad \hat{x} = \frac{x - v^* t}{\sqrt{2D^* t}}; \quad \hat{y} = \frac{y}{\sqrt{2D_T t}}.$$

For a Gaussian distribution with dispersion coefficients D^* and D_T/R in the longitudinal and transverse direction one would expect elliptic contour-lines. Figure 4, however, shows typical 'cigar'-shaped contours. It is clear that close to the original injection point (in Figure 4 around $\hat{x} = -2$) the particles have spend a relatively short time, τ, in the 'free' phase. During this time the particles displace not only very little in longitudinal direction, but also the spread in transverse direction is very limited. The result of this is that x displacement and y-spread are no longer independent, which is in contradiction to a truly Gaussian system. Also note that in the 1D case in Figure 2 the same parameters have been used and the corresponding distribution in x-direction comes out almost as a Gaussian curve (Figure 2, upper right graph).

4.2. **Longitudinal and transverse dispersion.** Analytical solutions including longitudinal and transverse dispersion have been obtained by [4], but not in a
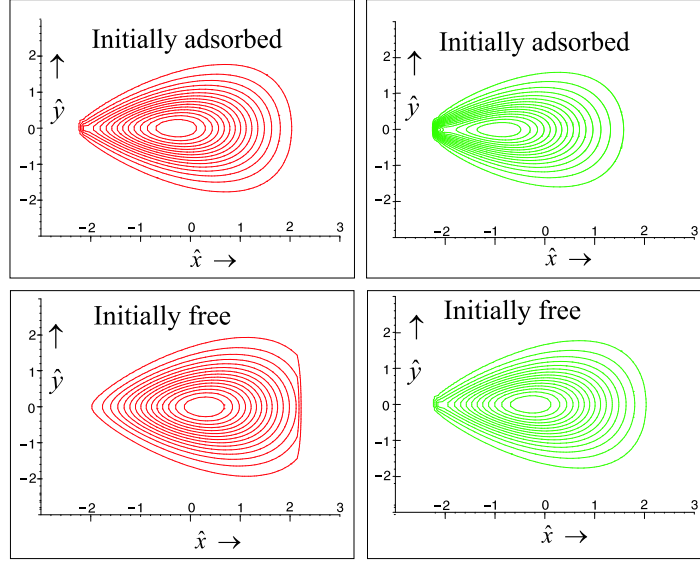
FIGURE 4. Contour-lines for free phase (red) and adsorbed phase (green) for several initial conditions. The symmetric case ($\lambda = 5$ and $\mu = 5$) at time $t = 1$.

closed-form. The integral expression by Carnahan is, in essence, equal to the one obtained by Van Kooten's approach:

$$(20) \qquad N_{ij}(x,y,t) = \frac{N_i^0}{\sqrt{D_L D_T}} \int_0^t \frac{h_{ij}(\tau,t)}{4\pi\tau} e^{-\frac{(x-v\tau)^2}{4D_L\tau} - \frac{y^2}{4D_T\tau}} \, d\tau$$

We apply expression (20) to evaluate the 'full' system (i.e, including advection, dispersion and sorption) using the following values: $\lambda = 0.2$, $\mu = 0$, $v = 1$, $D_L = 0.5$ and $D_T = 0.1$. The kinetics induced dispersion coefficient D^* now becomes 0.62, which is in the same order of magnitude as D_L.

The contour-lines in Figure 5 represent the distribution of the free phase for $t = 1$, $t = 20$ and $t = 150$, for the case of an initial pulse in equilibrium. Note that for longitudinal and transverse coordinate we have applied the same scaling as in Figure 4, (see (19)). At a short time ($t = 1$) almost circular contours occur, which suggests Gaussianity. At this stage microdispersion dominates the spreading process, which now progresses in a Gaussian way. At an intermediate time ($t = 20$) the 'cigar'-shaped contours start to develop. Here, we observe an increasing influence of the non Gaussian kinetics-induced dispersion. Finally, at large times ($t = 150$) the distribution becomes Gaussian again, with elliptic contours. The parameters of the early and late Gaussian distribution are quite different. For short times we have velocity v and dispersion coefficients D_L and D_T. For large times the velocity becomes v^* and dispersion coefficients $D_L/R + D^*$ and D_T/R for the longitudinal and transverse direction respectively. The early Gaussian distribution occurs because directly after the start of the pulse the effect of kinetic exchange between the phases is still small and the free phase consists mainly of particles that did not yet change their state. Therefore, they behave as a non-adsorbing solute.
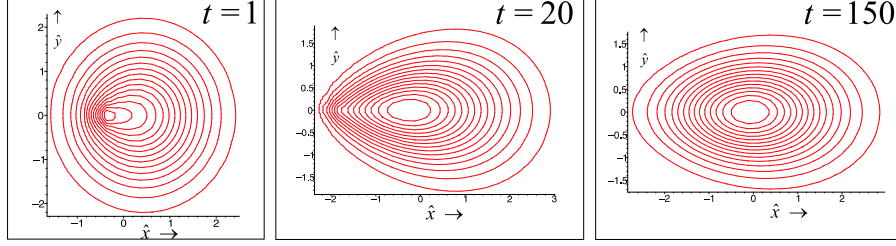
FIGURE 5. Full two-dimensional case. Distribution of the free phase at various times for an initial pulse in equilibrium; symmetric $\lambda = 0.2$ and $\mu = 0.2$; $D_L = 0.5$; $D_T = 0.1$; $v = 1$

As time goes on the influence of kinetics becomes more apparent and 'cigar' shaped contours develop.

5. MOMENT ANALYSIS

5.1. **One-dimensional.** The method of moments was introduced by [2], while studying the flow of solutes through a capillary tube (Taylor dispersion). Later, the method was successfully applied to solute transport in a layered porous medium by [25]. For contaminant transport with sorption the method was applied by [34], [35], [6] and [31]. These authors examine the asymptotic values of zero, first and second moments. Solutions for the entire pre-asymptotic regime of zeroth, first and second moments are derived by [27]. However, one of their expressions for the central second moment turns out to be incorrect. We copy here the formula (the $\oplus$ is a $+$), but should be a $-$) from [27], page 2136 for the normalized central moment, where the solute is in the free phase at time 0 *and* at time t :

$$
\sigma_{ff}^2 = \frac{t^2 A v^2 \beta \, (\beta - 1)^2}{(\beta + 1)^2 \, (1 + \beta \, A)^2} + t \left(\frac{2D}{\beta + 1} + \frac{2v^2 \beta}{k \, (\beta + 1)^3} \right)
$$
$$
+ tA \left(\frac{4v^2 \beta \, \left(-\beta^2 A - \beta^2 - \beta + 1 \right)}{k \, (1 + \beta \, A)^2 \, (\beta + 1)^3} \right) + tA \left(\frac{2D \, \beta \, (\beta - 1)}{(\beta + 1) \, (1 + \beta \, A)} \right)
$$
$$
+ \frac{2v^2 \beta \, (1 - A) \, \left(3\beta^2 A - 3 - \beta \, (A \oplus 1) \right)}{k^2 \, (1 + \beta \, A)^2 \, (\beta + 1)^4} + \frac{4D \, \beta \, (1 - A)}{k \, (1 + \beta \, A) \, (\beta + 1)^2}.
$$

Here Michalak and Kitanidis abbreviate $A = A(t) = \exp(-(\beta + 1)kt)$, and use the notation

$$
k = \mu, \quad \beta = \lambda/\mu.
$$

By giving the expressions for σ_{ff}^2, σ_{fa}^2, σ_{af}^2 and σ_{aa}^2 Michalak and Kitanides suggest that these expressions may be used to obtain variances for a general initial condition, by linearity. However, such a superposition can only be composed for the non-centralized moments. At large times the first and second moment appear to increase at a constant rate, which suggest that there exist an effective velocity v_e and effective dispersion coefficient D_e:

$$
v_e = \frac{\mu}{\lambda + \mu} v, \qquad D_e = \frac{\lambda \mu}{(\lambda + \mu)^3} v^2 + \frac{\mu}{\lambda + \mu} D.
$$

5.2. **Two-dimensional.** The 2D case is described by the equations (16). We may distinguish two different type of moments. The first type is that of the marginal moments, or moments with respect to the x-coordinate ignoring the information on the y-coordinates of the particles. The second type consist of conditional moments, either a moment with respect to x for a given value of y, or a moment with respect to the y and for a given value of x. Interestingly, the marginal moments for the 2D case are identical to the moments for the 1D case. In the following subsections we discuss the conditional moments.

5.2.1. *The x-moments conditioned on y.* This category of moments represent expected values of x^n for a population of particles with a specific y-coordinate. Note that these moments are a function of y. We define these moments as:

$$M_f^{(n)}(y) = \int\limits_{-\infty}^{+\infty} x^n N_f(x,y)\,\mathrm{d}x, \quad \text{and } M_a^{(n)}(y) = \int\limits_{-\infty}^{+\infty} x^n N_a(x,y)\,\mathrm{d}x$$

For $n = 0$ the expressions represent for each phase the particle distribution along the y-direction (the total mass of particles with the specified y-coordinate). Note that the higher order moments ($n > 0$) are not yet divided by the zeroth moment, so higher order moments are not normalized. For the initial condition we consider a (unit) pulse with the phases in equilibrium. Then, the two-dimensional particle distribution becomes:

$$(21) \qquad N_i^{eq}(x,y) = \int_0^t h_i^{eq}(\tau,t) \frac{\mathrm{e}^{-\frac{(x-v\tau)^2}{4D_L\tau} - \frac{y^2}{4D_T\tau}}}{4\pi\tau\sqrt{D_L D_T}}\,\mathrm{d}\tau$$

where i is a or f. This expression is obtained by applying (20), replace h_{ij} by h_i^{eq} (see (15)) and take N_i^0 equal to 1. For the equilibrium initial condition the moments are:

$$M_i^{(n)}(y) = \int\limits_{-\infty}^{+\infty} x^n N_i^{eq}(x,y)\,\mathrm{d}x$$

When we use (21) and change the order of integration, the zeroth, first and second moments become:

$$(22) \qquad M_i^{(0)}(y) = \int_0^t h_i^{eq}(\tau,t) \frac{\mathrm{e}^{-\frac{y^2}{4D_T\tau}}}{2\sqrt{\pi D_T}\,\tau}\,\mathrm{d}\tau$$

$$(23) \qquad M_i^{(1)}(y) = \int_0^t v\tau\, h_i^{eq}(\tau,t) \frac{\mathrm{e}^{-\frac{y^2}{4D_T\tau}}}{2\sqrt{\pi D_T}\,\tau}\,\mathrm{d}\tau$$

$$(24) \qquad M_i^{(2)}(y) = \int_0^t (2D_L\tau + v^2\tau^2) h_i^{eq}(\tau,t) \frac{\mathrm{e}^{-\frac{y^2}{4D_T\tau}}}{2\sqrt{\pi D_T}\tau}\,\mathrm{d}\tau.$$

Figure 6 shows the distribution along the y-axis for the zeroth moments of free and adsorbed phase for several times. The initial condition here is the equilibrium situation. The zeroth moment is plotted horizontally. The figure shows that particles of both phases gradually spread out in y-direction. Note in the figure at the right hand side that at t=5 the adsorbed phase is concentrated along $y = 0$ and
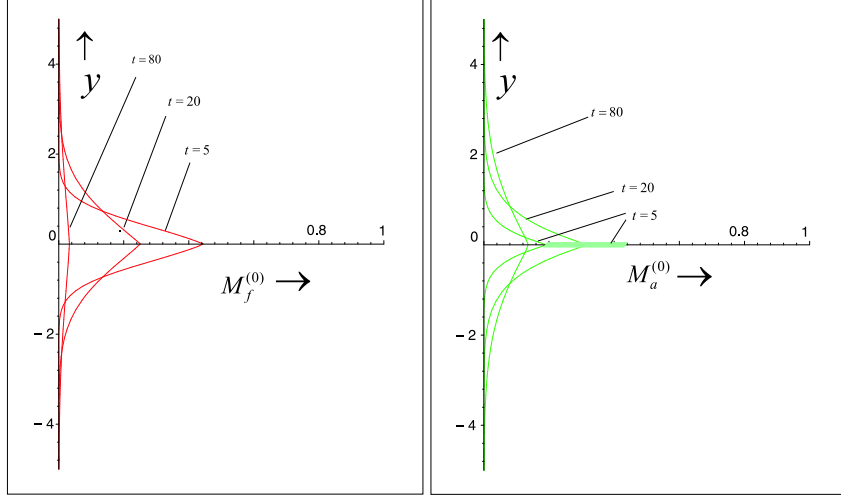
FIGURE 6. Zeroth moments as given by (22) versus y for t=5,20,80, left free phase, right adsorbed phase; $\lambda = \mu = 0.05$; D_T =0.03. Zeroth moment on the horizontal axis. In the figure at the right hand side the curve for t=5 has a pulse-shaped component $\delta(y)$ at y=0.

the curve has a pulse-shaped component $\delta(y)$ for y=0. This pulse represents the particles that did not yet spend time in the free phase and are still in the initial position. At larger times most adsorbed particles do have spent time in the free phase and the spreading in y-direction becomes visible.

Figure 7 shows the first moment for the free phase. The first moment, plotted horizontally, can be interpreted as the average distance travelled in the x-direction for the particles with a specific y-coordinate. As it appears, for $y = 0$ the first moments are smaller than for values of y greater or smaller than 0. It is an alternative illustration of the tailing effect. Particles spending less time in the free phase have less opportunity to displace in the x-direction and spread in the y-direction. Thus, a considerable fraction of these particles are found around the point of origin. Further away from the y-axis particles occur that have been able to disperse laterally. Therefore, they did spend some time in the free phase and, consequently, were also displaced further along the x-axis. Once more, we conclude that displacements in x- and y-direction are mutually dependent. This dependence in the spreading pattern is non-Gaussian.

5.2.2. *The y-moments, conditioned on x.* The y-moments conditioned on x are defined as:

$$M_f^{(m)}(x) = \int\limits_{-\infty}^{\infty} y^m N_f(x, y) \, \mathrm{d}y, \quad \text{and} \quad M_a^{(m)}(x) = \int\limits_{-\infty}^{\infty} y^m N_a(x, y) \, \mathrm{d}y,$$

We analyze the y-moments by the Laplace Transform using the following initial conditions:

$$N_f(x, y, t)|_{t=0} = \pi_f \delta(x)\delta(y), \quad \text{and} \quad N_a(x, y, t)|_{t=0} = \pi_a \delta(x)\delta(y)$$
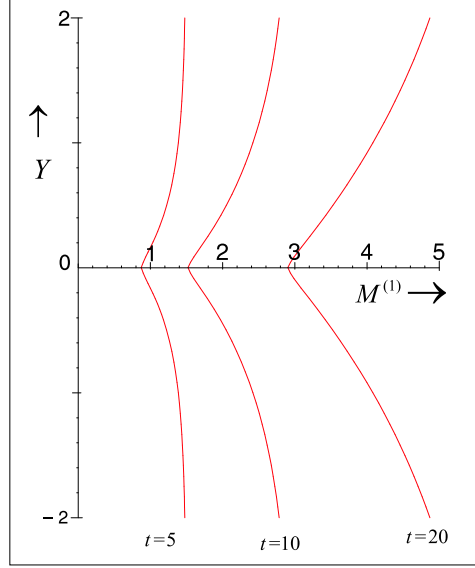
FIGURE 7. First moments for free phase versus y from (23) for $t = 5, 10, 20$. Numerical values: $\lambda = 0.05$; $\mu = 0.05$; $v = 0.3$; $D_L = 0.3$; $D_T = 0.03$. First moment on the horizontal axis.

After applying the Laplace transform to eq (16) and eliminating the transform of N_a we obtain the following differential equation:

$$D_L \frac{\partial^2 \widehat{N}_f}{\partial x^2} + D_T \frac{\partial^2 \widehat{N}_f}{\partial y^2} - v \frac{\partial \widehat{N}_f}{\partial x} - sb\widehat{N}_f + b\pi_f \delta(x)\delta(y) = 0$$

where $\widehat{N}_f$ denotes the particle density in Laplace space, s is the Laplace parameter and b is an expression depending on s:

$$b = \frac{s + \lambda + \mu}{s + \mu}$$

$\widehat{N}_a$ is related to $\widehat{N}_f$ by (see eq. (16)): $(s + \mu)\widehat{N}_a - \pi_a\delta(x)\delta(y) = \lambda\widehat{N}_f$.

After taking the moments with respect to y we find for the zeroth moment:

$$D_L \frac{\partial^2 \widehat{M}_f^{(0)}}{\partial x^2} - v \frac{\partial \widehat{M}_f^{(0)}}{\partial x} - sb\widehat{M}_f^{(0)} + b\pi_f \delta(x) = 0$$

$$\widehat{M}_a^{(0)} = \frac{\lambda}{s + \mu}\widehat{M}_f^{(0)} + \frac{\pi_a}{s + \mu}\delta(x)$$

The solution for $\widehat{M}_f^{(0)} = \widehat{M}_f^{(0)}(x)$ is

$$\widehat{M}_f^{(0)} = \frac{b\pi_f}{\sqrt{v^2 + 4bsD_L}} \exp\left(\frac{xv - |x|\sqrt{v^2 + 4bsD_L}}{2D_L}\right)$$

where we use that the concentrations are zero at $x = \pm\infty$. The inverse can be found with numerical Laplace inversion algorithms [8], [32], [1], and is shown in Figure 8.
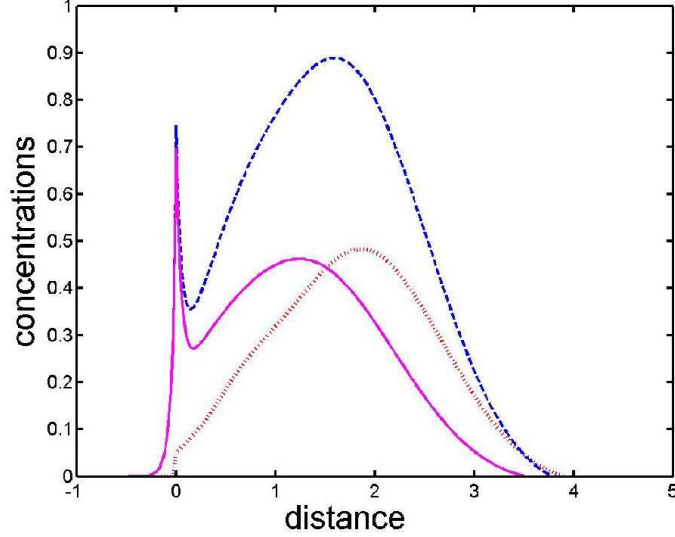
FIGURE 8. *Zeroth moment for total concentration $M^{(0)}$ (dashed),
free concentration $M_f^{(0)}$ (dotted) and adsorbed $M_a^{(0)}$ concentration
(drawn). Small numerical inaccuracies lead to the fact that the
zeroth moment for the total concentration is below the curve for the
free concentration. The peaks at $x = 0$, representing the function
$\delta(x)$ are "approximated" by two exponential curves for reasons of
illustration.*

For the second moment we obtain the equations:

$$D_L \frac{\partial^2 \widehat{M}_f^{(2)}}{\partial x^2} - v \frac{\partial \widehat{M}_f^{(2)}}{\partial x} - sb\widehat{M}_f^{(2)} + 2D_T \widehat{M}_f^{(0)} = 0, \text{ and } s\widehat{M}_a^{(2)} = \lambda \widehat{M}_f^{(2)} - \mu \widehat{M}_a^{(2)}$$

where we use that $\displaystyle\int_{-\infty}^{\infty} y^2 \frac{\partial^2 \widehat{N}_f}{\partial y^2} \, \mathrm{d}y = \widehat{M}_f^{(0)}$, with the solution:

$$\widehat{M}_f^{(2)}(x) = b\pi_f \frac{\mu^2 D_L}{\lambda + \mu} \frac{\exp\left(\frac{xv - x\sqrt{v^2 + 4bsD_L}}{2D_L}\right)}{v^2 + 4bsD_L} \times \frac{\mu}{v}\left(x + \frac{2D_L}{\sqrt{v^2 + 4bsD_L}}\right), \text{ for } x > 0,$$

and $\widehat{M}_a^{(2)}(x) = \dfrac{\lambda}{s + \mu} \widehat{M}_f^{(2)}(x)$.

The ratio of the numerically [32] inverted $\widehat{M}_f^{(2)}$ and $\widehat{M}_f^{(0)}$ is the normalized and
centralized second moment (conditioned on x) and this ratio turns out to be x/Pe.
Thus, the lateral spread depends on x, which (again) explains the tailing and the
previously observed 'cigar shape'.

6. CONCLUSIONS

We discuss a stochastic particle approach, considering a particle that changes
between a mobile and immobile state governed by a Markov chain, while its spatial
displacement is governed by a random walk. Generally, particle models are assumed

to describe the advective-dispersive-kinetic transport process correctly, but in the literature a rigorous proof is lacking. Our analysis shows that it is possible to derive the correct set of differential equations from a stochastic model for a single particle. To examine the non-Gaussian nature of the spreading process we analyze first the telegrapher's equation. This equation arises when only advection and kinetic sorption is considered. We show that in such a system an apparent dispersion process occurs, generated only by the kinetic changing of the particle in states with different velocities (i.e. *zero* or v). This 'kinetics-induced' dispersion is non-Gaussian for short and intermediate times, while at large times the process develops as Gaussian dispersion. When hydrodynamic dispersion is included again, the spreading process becomes a combination of a Gaussian and non-Gaussian dispersion. We illustrate this for the 2D case. At short times the process is Gaussian, since hydrodynamic dispersion is the dominating process. At intermediate times the influence of kinetic induced dispersion increases and the spreading becomes non-Gaussian. Finally, at large times the dispersion becomes Gaussian again, but the (effective) longitudinal dispersion coefficient has an additional term due to the kinetics. Moveover, we find for the 2D case that the transverse spreading depends on the longitudinal coordinate, resulting in 'cigar-shaped' contours. The mechanism is best illustrated when longitudinal dispersion is assumed zero. Here the particles displace in the x-direction by advection and spread transversely by dispersion. Particles spending more time in the adsorbed phase are displaced less in x-direction, and also less spread out in y-direction. In a truly Gaussian distribution the transverse spreading is independent of the longitudinal coordinate. When longitudinal dispersion is included the same effect is observed, although for short times (compared to the kinetic exchange rate) the situation is now dominated by hydrodynamic dispersion. With respect of the validity of effective properties (velocity and dispersion), we conclude the following. The velocity and dispersion coefficients are represented by the rate of increase of the first and centralized second moment (times $1/2$). For cases with low adsorption and desorption rates, the rates of increase for the moments remain time dependent for a relatively long time. We conclude that constant effective properties can not be defined directly after the start of solute injection. For large times an asymptotic behavior is observed with a constant mean displacement and rate of dispersion, while the third moment vanishes and the kurtosis approaches a value of 3. This can be proved via our stochastic model by applying a sophisticated version of the Central Limit Theorem (Section 2.2). The critical time, required before dispersion coefficients becomes constant, is in the order of $3/(\lambda + \mu)$. The effective velocity is $v\mu/(\lambda + \mu)$, similar to the case of linear equilibrium adsorption. However, at early times the free particles move with the original groundwater velocity and build up a lead with respect to the adsorbed phase. In the asymptotic stage, the adsorbed and free particles displace with the same average velocity, but the lead of the free plume is maintained. The effective longitudinal dispersion, can be much higher than in the case of linear equilibrium adsorption. The additional term, $v^2\lambda\mu/(\lambda + \mu)^3$ depends also on the groundwater velocity. It is remarkable that it depends on v^2, while the micro-scale dispersion is linear in v.

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